

Relation of the Force Constant of a Bond to the Electric Field at a Nucleus

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ABSTRACT: The change in the electric field at a nucleus in a molecule due to bond stretch is related to the force constant of the stretched bond. The validity of this relationship using approximate wave functions at the SCF and MP2 levels of theory is tested for the diatomic molecules H_2 , HF, CO, and N_2 . The effect of basis set variation on H_2 is also investigated. © 1997 John Wiley & Sons, Inc. *J Comput Chem* **18**: 1664–1667, 1997

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Introduction

The effect of external electric fields on the local electric field at each nucleus in a molecule has been used previously to determine various molecular properties.^{1–5} The connection between various electric nuclear shielding tensors, which are a measure of the extent to which the nucleus in a molecule is shielded from external fields, and geometry derivatives of permanent molecular multipole moments, polarizabilities, and hyperpolarizabilities, has been established in the literature.^{2–5}

In this article, the bond length dependence of the electric field at a nucleus in a molecule (in the absence of external electric fields) is related to the stretching force constant of a bond in the molecule.

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Although the expression obtained is applicable to any molecule in general, we restrict our study to the diatomic molecules H_2 , HF, CO, and N_2 as test examples.

The numerical values for the electric field at the nucleus and the bond force constant are calculated by *ab initio* methods at the SCF and MP2 levels of theory using the CADPAC suite of programs.⁶ Computation of the electric fields at the nuclei of a molecule involve analytical single-point calculations of one-electron properties, whereas determination of the force constant of the bond involves a more costly evaluation of the analytical second derivatives of the potential surface with respect to nuclear displacement.

The purpose of this article is to test the validity of this relationship in computing the force constant of the bonds in the molecules using suitable basis functions (i.e., directly via analytic second derivatives and indirectly through the calculation of the

one-electron properties). The agreement between the two approaches is also examined by systematically improving the basis sets on H₂.

Theory

The derivative of the energy of a molecule with respect to a nuclear displacement, R_{α_A} , of nucleus A along the α Cartesian coordinate can be obtained from the Hellmann–Feynman theorem^{7,8}:

$$\begin{aligned}\partial E / \partial R_{\alpha_A} &= \partial \langle \psi^0 | \hat{H} | \psi^0 \rangle / \partial R_{\alpha_A} \\ &= \langle \psi^0 | \partial \hat{H} / \partial R_{\alpha_A} | \psi^0 \rangle \\ &\quad + \langle \psi^0 | \hat{H} | \partial \psi^0 / \partial R_{\alpha_A} \rangle \\ &\quad + \langle \partial \psi^0 / \partial R_{\alpha_A} | \hat{H} | \psi^0 \rangle \\ &= \langle \psi^0 | \partial \hat{H} / \partial R_{\alpha_A} | \psi^0 \rangle\end{aligned}\quad (1)$$

where ψ^0 represents an exact, normalized eigenfunction and \hat{H} is the Born–Oppenheimer molecular electronic Hamiltonian. In this case, the derivative $\partial E / \partial R_{\alpha_A}$ is the force on nucleus A and is equal to the product of the nuclear charge, Z_A , and the field at the nucleus, $f_{\alpha}^{(0)A}$, due to all other charges in the molecule³:

$$\frac{\partial E}{\partial R_{\alpha_A}} = Z_A f_{\alpha}^{(0)A} \quad (2)$$

In the absence of external electric fields, the electric field at the nucleus is directly related to the gradient of the potential surface with respect to a displacement of the nucleus³:

$$f_{\alpha}^{(0)A} = -\frac{1}{Z_A} \frac{\partial V}{\partial R_{\alpha_A}} \quad (3)$$

and is consequently zero at the equilibrium geometry. Because the Hellman–Feynman theorem is not well-satisfied by approximate wave functions the field at the nucleus when the molecule is in its equilibrium geometry is not exactly zero but some value close to zero and dependent on the quality or completeness of the basis functions.

Taking the derivative of eq. (3) with respect to motion of nucleus B along an axis β yields:

$$\frac{\partial f_{\alpha}^{(0)A}}{\partial R_{\beta_B}} = -\frac{1}{Z_A} \frac{\partial^2 V}{\partial R_{\alpha_A} \partial R_{\beta_B}} \quad (4)$$

Similarly:

$$\frac{\partial f_{\beta}^{(0)B}}{\partial R_{\alpha_A}} = -\frac{1}{Z_B} \frac{\partial^2 V}{\partial R_{\beta_B} \partial R_{\alpha_A}} \quad (5)$$

Because the order of differentiation in the second derivative of the potential surface does not matter then it follows from eqs. (4) and (5) that:

$$Z_A \frac{\partial f_{\alpha}^{(0)A}}{\partial R_{\beta_B}} = Z_B \frac{\partial f_{\beta}^{(0)B}}{\partial R_{\alpha_A}} \quad (6)$$

that is, we obtain an expression relating the change (with nuclear displacement) of the electric field at one nucleus to that of the other nucleus comprising the bond.

The derivative of the electric field at nucleus A with respect to a displacement of the same nucleus is given by:

$$\frac{\partial f_{\alpha}^{(0)A}}{\partial R_{\alpha_A}} = -\frac{1}{Z_A} \frac{\partial^2 V}{\partial R_{\alpha_A}^2} \quad (7)$$

Considering A—B to represent a diatomic molecule with nucleus A at the origin of a Cartesian coordinate system and nucleus B lying on the positive z axis, and noting that $\partial^2 V / \partial R_{z_A}^2 = \partial^2 V / \partial R_{z_B}^2 = k_{AB}$ (the force constant of the bond A—B) and $\partial f_z^{(0)A} / \partial R_{z_A} = -\partial f_z^{(0)A} / \partial R_{z_B}$, yields:

$$Z_A \frac{\partial f_z^{(0)A}}{\partial R_{z_B}} = \frac{\partial^2 V}{\partial R_{z_A}^2} = k_{AB} \quad (8)$$

This equation implies that the force constant of the bond can be determined by simply computing $f_z^{(0)A}$ at two displacements of the bond about its equilibrium bond length and evaluating the derivative by numerical finite differences.

Results

As mentioned previously, the derivative $\partial f_z^{(0)A} / \partial R_{z_B}$ may be determined by two *ab initio* calculations of the electric field at the nucleus A (in the absence of applied electric fields) for bond lengths $r_e + \delta$ and $r_e - \delta$, where r_e is the *ab initio* equilibrium bond length and δ is a small displacement of nucleus B along the positive z axis, leading to:

$$\frac{\partial f_z^{(0)A}}{\partial R_{z_B}} = \frac{f_z^{(0)A}(r_e + \delta) - f_z^{(0)A}(r_e - \delta)}{2\delta} \quad (9)$$

with a value of 0.005 atomic units selected for δ . The force constant, k_{AB} , for the A—B bond at its *ab initio*-optimized bond length was computed by analytic second derivative calculations at both the SCF and MP2 levels of theory and is computationally more expensive than the finite differences procedure. All computations were performed by the CADPAC suite of programs.⁶

Polarized double-zeta basis sets available from the CADPAC library⁶ (designated as the POLDZ basis set) were used for the H, C, N, O, and F atoms, giving a total of 16 and 44 basis functions for H₂ and HF, and 72 basis functions for CO and N₂. These basis sets are generated from the Dunning double-zeta basis by adding the derivatives of all the basis functions. Previously, they have been found to satisfy the Hellmann–Feynman theorem well for dipole and quadrupole derivatives and electric nuclear shielding tensors.^{4,9}

Inspection of Table I shows that the relationship given by eq. (8) holds well for the diatomic molecules H₂, HF, CO, and N₂ at the SCF level, with the largest discrepancy between the left-hand side and the right-hand side of eq. (8) being -2.0% for H₂, and the smallest 1.5% for HF. So, even with the small basis set on H₂, the change of the electric field at the nucleus, due to an extension of the H₂ bond, can provide a good estimate of the stretching force constant of the bond.

The relationship given by eq. (6) holds fairly well for the heteroatomic molecules and will be obeyed exactly in the limit of basis set completeness. Because of symmetry this relationship holds

exactly for the homonuclear diatomics (see Table I).

The results obtained at the MP2 level are not as satisfactory as those for the SCF but still provide a reasonable estimate of the force constant k_{AB} . The MP2 values for the bond force constant are typically less than the corresponding SCF values, with the discrepancy between the direct (through analytic second derivatives) and the indirect (through the derivative of the electric field at the nucleus) methods being largest for the isoelectronic molecules CO and N₂. However, the agreement between the two approaches is still reasonable and may possibly be improved by using larger basis sets to describe the electron correlation, especially within the multiple-bonded molecules CO and N₂.

A basis set study of the H₂ molecule was undertaken to determine whether agreement between the calculated quantities, $\partial f_z^{(0)A} / \partial R_{z_B}$ and k_{AB} , could be improved by augmenting the original POLDZ set with more diffuse sets of *p* functions and the addition of *d* functions. The results are shown in Table II and clearly indicate that, at both SCF and MP2 levels, excellent agreement is achieved by systematically adding two sets of *p* primitives (with exponents of 0.0411 and 0.0137) and two sets of *d* primitives (with exponents of 0.9 and 0.3) to the initial POLDZ set for each H atom, thereby gradually increasing the total number of basis functions on H₂ from 16 to a maximum of 34 basis functions.

Indeed, the discrepancy between the two approaches is reduced to a magnitude of less than

TABLE I.
SCF and MP2 *Ab Initio* Values for the Equilibrium Bond Length (r_e), $Z_A \partial f_z^{(0)A} / \partial R_{z_B}$, $Z_B \partial f_z^{(0)B} / \partial R_{z_A}$ and the Force Constant (k_{AB}) for Diatomic Molecules A—B, Where the Nucleus of A Is at the Origin and the Nucleus of B Lies on the Positive *z* Axis.^a

Molecule	r_e	$Z_A \partial f_z^{(0)A} / \partial R_{z_B}$	$Z_B \partial f_z^{(0)B} / \partial R_{z_A}$	k_{AB}	% Diff.
SCF					
H ₂	1.4107	0.394	0.394	0.402	-2.0
HF	1.7067	0.697	0.693	0.686	1.5
CO	2.0922	1.490	1.475	1.465	1.7
N ₂	2.0241	1.907	1.907	1.876	1.6
MP2					
H ₂	1.4221	0.376	0.376	0.386	-2.4
HF	1.7486	0.589	0.594	0.576	2.2
CO	2.1562	1.144	1.126	1.095	4.5
N ₂	2.1191	1.204	1.204	1.143	5.3

^aIn HF, the F atom is at the origin and in CO the C atom is at the origin. Polarized double-zeta (POLDZ) basis sets are used for all atoms. % Diff. = $((Z_A \partial f_z^{(0)A} / \partial R_{z_B} - k_{AB}) / k_{AB}) \times 100\%$. All quantities are in atomic units.

TABLE II.
Variation (with Basis Set) of SCF and MP2 *Ab Initio*
Values for Equilibrium Bond Length (r_e),
 $Z_H \partial f_z^{(0)H_A} / \partial R_{z_{H_B}}$ **and the Force Constant (k_{AB})**
of the H_2 Molecule, Where the Molecule is
Represented as $H_A - H_B$, with H_A to H_B Being the
Positive z Direction.^a

Basis	$Z_H \partial f_z^{(0)H_A} / \partial R_{z_{H_B}}$	k_{AB}	% Diff.
SCF			
(1)	0.4021	0.3941	2.0
(2)	0.4015	0.3934	2.0
(3)	0.3978	0.4001	-0.6
(4)	0.3984	0.3969	0.4
MP2			
(1)	0.3760	0.3854	-2.4
(2)	0.3755	0.3848	-2.4
(3)	0.3878	0.3861	0.4
(4)	0.3848	0.3857	-0.2

Basis (1): POLDZ + $1p(0.0411)$; basis (2): basis (1) + $1p(0.0137)$; basis (3): basis (2) + $1d(0.9)$; basis (4): basis (3) + $1d(0.3)$.

^aThe change in the electric field at the nucleus of H_A (in the absence of external fields) due to a displacement of the nucleus of H_B along the z axis is denoted by $\partial f_z^{(0)H_A} / \partial R_{z_{H_B}}$. % Diff = $((Z_H \partial f_z^{(0)H_A} / \partial R_{z_{H_B}} - k_{AB}) / k_{AB}) \times 100\%$. The basis sets described are formed from the original POLDZ basis sets by addition of p and d derivatives with the exponents shown. All quantities are in atomic units.

0.5% with the largest basis set, which is in fact only a moderately small basis set. Therefore, it is clear that the relationship given by eq. (8) is well satisfied at SCF and MP2 even by basis sets of moderate size.

Conclusion

It has been shown that the relationship given by eq. (8) can be used to predict the force constant of the bond in a diatomic molecule by evaluation of the change in the electric field at the nucleus (in the absence of external fields) due to the extension of the bond.

This method is suitable for both SCF and MP2 calculations and excellent agreement with force constants calculated directly via a full analytic second derivative computation of the potential surface with respect to nuclear displacement can be achieved. Improved agreement between the two approaches is possible if suitably large basis sets

are employed, as shown by the basis set study of H_2 (Table II). However, the indirect method has the advantage of being much less computationally demanding than the direct method.

It should be noted that even though the indirect method for the computation of the force constant [via eq. (8)] has been applied here only to diatomic molecules it is possible [via eq. (7)] to compute the force constant of bonds in polyatomic molecules by this method. In this case, the fact that the force constants of polyatomics also arise from angle changes (bending motions, torsion), which are not treated by this theory, must be taken into account. However, it is debatable whether the indirect method is computationally competitive with a direct analytic second-derivative calculation for polyatomics, because the indirect method would involve finite difference calculations for every bond in the molecule, whereas the analytic method computes the force constants for all bonds at the same time.

It may be possible to use relationships of the sort discussed here to study the changes in the electric field at selected nuclei in polyatomic molecules due to the displacement or perturbation of neighboring bonds. Future work will be concerned with the investigation of these ideas and application to considerably larger molecular systems.

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